ADDITIVE COMPOSITION FOR TRANSMISSION OIL CONTAINING HYDRATED ALKALI METAL BORATE AND HEXAGONAL BORON NITRIDE

Field of the Invention

This invention is directed to an additive composition for a transmission oil. More particularly, this invention is directed to an additive composition comprising an oil dispersion of a hydrated alkali metal borate and an oil dispersion of hexagonal boron nitride, as well as lubricating oil compositions containing the same.

References

The following references are cited in this application as superscript numbers:

[1] Peeler, U.S. Patent No. 3,313,727, *Alkali Metal Borate E.P. Lubricants*, issued April 11, 1967

[2] Adams, U.S. Patent No. 3,912,643, *Lubricant Containing Neutralized Alkali Metal Borates*, issued October 14, 1975

[3] Sims, U.S. Patent No. 3,819,521, *Lubricant Containing Dispersed Borate and a Polyol*, issued June 25, 1974

[4] Adams, U.S. Patent No. 3,853,772, *Lubricant Containing Alkali Metal Borate Dispersed with a Mixture of Dispersants*, issued December 10, 1974

[5] Adams, U.S. Patent No. 3,997,454, *Lubricant Containing Potassium Borate*, issued December 14, 1976

[6] Adams, U.S. Patent No. 4,089,790, *Synergistic Combinations of Hydrated Potassium Borate, Antiwear Agents, and Organic Sulfide Antioxidants*, issued May 16, 1978

[7] Adams, U.S. Patent No. 4,163,729, *Synergistic Combinations of Hydrated Potassium Borate, Antiwear Agents, and Organic Sulfide Antioxidants*, issued August 7, 1979

[8] Frost, U.S. Patent No. 4,263,155, *Lubricant Composition Containing an Alkali Metal Borate and Stabilizing Oil-Soluble Acid,* issued April 21, 1981

[9] Frost, U.S. Patent No. 4,401,580, *Lubricant Composition Containing an Alkali Metal Borate and an Ester-Polyol Compound,* issued August 30, 1983

[10] Frost, U.S. Patent No. 4,472,288, *Lubricant Composition Containing an Alkali Metal Borate and an Oil-Soluble Amine Salt of a Phosphorus Compound,* issued September 18, 1984

[11] Clark, U.S. Patent No. 4,534,873, *Automotive Friction Reducing Composition,* issued August 13, 1985

[12] Brewster, U.S. Patent No. 3,489,619, *Heat Transfer and Quench Oil*, issued January 13, 1970.

[13] Salentine, U.S. Patent No. 4,717,490, *Synergistic Combination of Alkali Metal Borates, Sulfur Compounds, Phosphites and Neutralized Phosphate,* issued January 5, 1988

All of the above patents are herein incorporated by reference in their entirety to the same extent as if each individual patent was specifically and individually indicated to be incorporated by reference in its entirety.

State of the Art

High load conditions often occur in gear sets such as those used in automobile transmissions and differentials, pneumatic tools, gas compressors, centrifuges, high-pressure hydraulic systems, metal working and similar devices, as well as in many types of bearings. When employed in such environments, it is conventional to add an extreme-pressure (E.P.) agent to the lubricant composition and, in this regard, alkali metal borates are well known extreme-pressure agents for such compositions.[1-11, 13] E.P. agents are added to lubricants to prevent destructive metal-to-metal contact in the lubrication of moving surfaces. While under normal conditions termed "hydrodynamic", a film of lubricant is maintained between the relatively moving surfaces governed by lubricant parameters, and principally viscosity. However, when load is increased, clearance between the surfaces is reduced, or when speeds of moving surfaces are such that the film of oil cannot be maintained, the condition of "boundary lubrication" is reached; governed largely by the parameters of the contacting surfaces. At still more severe conditions, significant destructive contact

manifests itself in various forms such as wear and metal fatigue as measured by ridging and pitting. It is the role of E.P. additives to prevent this from happening. For the most part, E.P. agents have been oil soluble or easily dispersed as a stable dispersion in the oil, and largely have been organic compounds chemically reacted to contain sulfur, halogen (principally chlorine), phosphorous, carboxyl, or carboxylate salt groups which react with the metal surface under boundary lubrication conditions. Stable dispersions of hydrated alkali metal borates have also been found to be effective as E.P. agents.

Moreover, because hydrated alkali metal borates are insoluble in lubricant oil media, it is necessary to incorporate the borate as a dispersion in the oil and homogenous dispersions are particularly desirable. The degree of formation of a homogenous dispersion can be correlated to the turbidity of the oil after addition of the hydrated alkali metal borate with higher turbidity correlating to less homogenous dispersions. In order to facilitate formation of such a homogenous dispersion, it is conventional to include a dispersant in such compositions. Examples of dispersants include lipophilic surface-active agents such as alkenyl succinimides or other nitrogen containing dispersants as well as alkenyl succinates.[1-4, 12] It is also conventional to employ the alkali metal borate at particle sizes of less than 1 micron in order to facilitate the formation of the homogenous dispersion.[11]

In addition, anti-sticking agents are often employed in automotive gear boxes to provide smooth synchronization and good shiftability. Examples of such anti-sticking agents include phosphates, phosphites, phosphionates, thiophosphates, carbamates, molybdenum dithiocarbamates and dithiophosphates.

It is also known that boron nitride exhibits friction modifying properties in lubricants. For example, U.S. Patent No. 4,787,993, issued November 29, 1988 to Nagahiro, discloses a lubricant effective for the reduction of friction which comprises dispersing a finely powdered aromatic or polyamide resin into a fluid fat or oil, which may additionally contain molybdenum disulfide, organic molybdenum or boron nitride.

Furthermore, U.S. Patent No. 4,715,972, issued December 29, 1987 to Pacholke, discloses a solid lubricant additive for gear oils comprising solid lubricant particles combined with a stabilizing agent and a fluid carrier, wherein the solid lubricant particles are selected from the group consisting of molybdenum disulfide,

graphite, cerium fluoride, zinc oxide, tungsten disulfide, mica, boron nitrate, boron nitride, borax, silver sulfate, cadmium iodide, lead iodide, barium fluoride, tin sulfide, fluorinated carbon, PTFE, intercalated graphite, zinc phosphide, zinc phosphate, and mixtures thereof. This patent further discloses that such lubricant additive provides the gear oil with improved demulsibility, stability and compatibility characteristics of the gear oil when contaminated with water.

Accordingly, it is an object of the present invention to provide a lubricant additive composition having good anti-sticking properties when used in transmission oils.

SUMMARY OF THE INVENTION

The present invention provides a novel additive composition for a transmission oil comprising:

(a) an oil dispersion of a hydrated alkali metal borate; and

(b) an oil dispersion of hexagonal boron nitride;

wherein the weight ratio of the hydrated alkali metal borate to the hexagonal boron nitride is in the range of about 95:5 to about 5:95.

The additive composition of the present invention may be suitably employed in both manual transmission gear oils and automatic transmission oils. Preferably, the additive composition will be employed in a manual transmission gear oil.

The present invention further provides a lubricating oil composition comprising a major amount of a transmission oil of lubricating viscosity and an effective synchronizer sticking reducing amount of the additive composition described above. Preferably, the transmission oil is a manual transmission gear oil.

Among other factors, the present invention is based in part upon the surprising discovery that the unique combination of an oil dispersion of a hydrated alkali metal borate and an oil dispersion of hexagonal boron nitride provides a significant and unexpected reduction in synchronizer sticking when used as an additive composition in a manual transmission gear oil.

DETAILED DESCRIPTION OF THE INVENTION

As noted above, the present invention is directed to a novel additive composition for a transmission oil comprising (a) an oil dispersion of a hydrated alkali metal borate, and (b) an oil dispersion of hexagonal boron nitride, wherein the

weight ratio of the hydrated alkali metal borate to the hexagonal boron nitride is in the range of about 95:5 to about 5:95.

Typically, the oil dispersion of hydrated alkali metal borate will contain a hydrated alkali metal borate, a dispersant, optionally a detergent, and an oil of lubricating viscosity. Preferably, the dispersant employed in the oil dispersion of hydrated alkali metal borate will be selected from the group consisting of a polyalkylene succinimide, a polyalkylene succinic anhydride, a polyalkylene succinic acid, a mono- or di-salt of a polyalkylene succinic acid, and mixtures thereof. Optionally, the oil dispersion of hydrated alkali metal borate will also contain a detergent, such as a metal sulfonate, preferably an alkylaromatic calcium sulfonate or other Group II metal sulfonate that acts in the present compositions to help provide for a homogeneous dispersion.

The oil dispersion of hydrated alkali metal borate preferably includes those compositions comprising from about 10 to 75 weight percent of the hydrated alkali metal borate; from about 2 to 40 weight percent of a dispersant; and from about 30 to 70 weight percent of an oil of lubricating viscosity, all based on the total weight of the oil dispersion.

Each of the components in the additive composition of the present invention will be described in further detail below.

THE HYDRATED ALKALI METAL BORATE

Hydrated alkali metal borates are well known in the art. Representative patents disclosing suitable borates and methods of manufacture include: U.S. Patent Nos. 3,313,727; 3,819,521; 3,853,772; 3,912,643; 3,997,454; and 4,089,790.[1-6]

The hydrated alkali metal borates suitable for use in the present invention can be represented by the following general formula:

$$M_2O \cdot xB_2O_3 \cdot yH_2O$$

wherein M is an alkali metal, preferably sodium or potassium; x is a number from 2.5 to 4.5 (both whole and fractional); and y is a number from 1.0 to 4.8. More preferred are the hydrated potassium borates, particularly the hydrated potassium triborates. The hydrated borate particles will generally have a mean particle size of less than 1 micron.

In the alkali metal borates employed in this invention, the ratio of boron to alkali metal will preferably range from about 2.5:1 to about 4.5:1.

Oil dispersions of hydrated alkali metal borates are generally prepared by forming, in deionized water, a solution of alkali metal hydroxide and boric acid, optionally in the presence of a small amount of the corresponding alkali metal carbonate. The solution is then added to a lubricant composition comprising an oil of lubricating viscosity, a dispersant and any optional additives to be included therein (e.g., a detergent, or other optional additives) to form an emulsion that is then dehydrated.

Because of their retention of hydroxyl groups on the borate complex, these complexes are referred to as “hydrated alkali metal borates” and compositions containing oil/water emulsions of these hydrated alkali metal borates are referred to as “oil dispersions of hydrated alkali metal borates”.

Preferred oil dispersions of alkali metal borates will have a boron to alkali metal ratio of about 2.5:1 to about 4.5:1. In another preferred embodiment, the hydrated alkali metal borate particles generally will have a mean particle size of less than 1 micron. In this regard, it has been found that the hydrated alkali metal borates employed in this invention preferably will have a particle size where 90% or greater of the particles are less than 0.6 microns.

In the oil dispersion of hydrated alkali metal borate, the hydrated alkali metal borate will generally comprise about 10 to 75 weight percent, preferably 25 to 50 weight percent, more preferably about 30 to 40 weight percent of the total weight of the oil dispersion of the hydrated borate. (Unless otherwise stated, all percentages are in weight percent.)

The additive compositions and lubricant compositions of this invention can further employ surfactants, detergents, other dispersants and other conditions as described below and known to those skilled in the art. Optionally, the additive compositions contain an alkylaromatic or polyisobutenyl sulfonate.

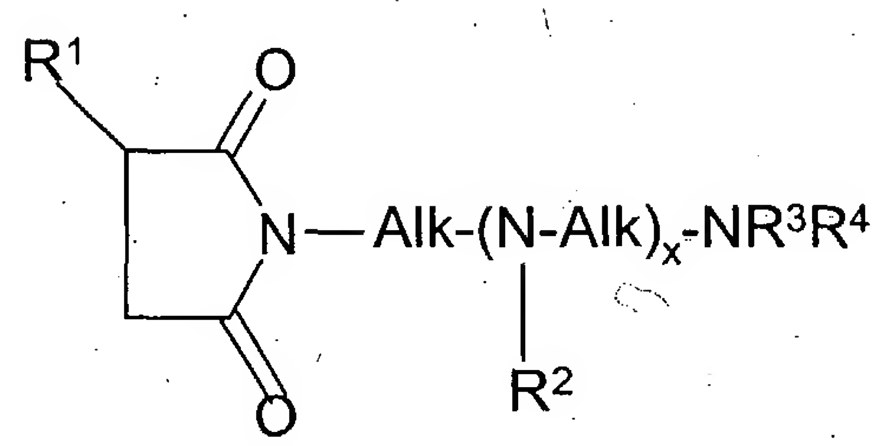
The oil dispersions of hydrated alkali metal borates employed in this invention generally comprise a dispersant, an oil of lubricating viscosity, and optionally a detergent, that are further detailed below.

THE DISPERSANT

The dispersant employed in the oil dispersion of hydrated alkali metal borate used in this invention can be ashless dispersants such as an alkenyl succinimide, an alkenyl succinic anhydride, an alkenyl succinate ester, and the like, or mixtures of such dispersants.

Ashless dispersants are broadly divided into several groups. One such group is directed to copolymers which contain a carboxylate ester with one or more additional polar function, including amine, amide, imine, imide, hydroxyl carboxyl, and the like. These products can be prepared by copolymerization of long chain alkyl acrylates or methacrylates with monomers of the above function. Such groups include alkyl methacrylate-vinyl pyrrolidinone copolymers, alkyl methacrylate-dialkylaminoethy methacrylate copolymers and the like. Additionally, high molecular weight amides and polyamides or esters and polyesters such as tetraethylene pentamine, polyvinyl polysterarates and other polystearamides may be employed. Preferred dispersants are N-substituted long chain alkenyl succinimides.

Alkenyl succinimides are usually derived from the reaction of alkenyl succinic acid or anhydride and alkylene polyamines. These compounds are generally considered to have the formula



wherein R^1 is a substantially hydrocarbon radical having a molecular weight from about 400 to 3000, that is, R^1 is a hydrocarbyl radical, preferably an alkenyl radical, containing about 30 to about 200 carbon atoms; Alk is an alkylene radical of 2 to 10, preferably 2 to 6, carbon atoms, R^2, R^3, and R^4 are selected from a C_1-C_4 alkyl or alkoxy or hydrogen, preferably hydrogen, and x is an integer from 0 to 10, preferably 0 to 3. The actual reaction product of alkylene succinic acid or anhydride and alkylene polyamine will comprise the mixture of compounds including succinamic acids and succinimides. However, it is customary to designate this reaction product as a

succinimide of the described formula, since this will be a principal component of the mixture. See, for example, U.S. Patent Nos. 3,202,678; 3,024,237; and 3,172,892.

These N-substituted alkenyl succinimides can be prepared by reacting maleic anhydride with an olefinic hydrocarbon followed by reacting the resulting alkenyl succinic anhydride with the alkylene polyamine. The R^1 radical of the above formula, that is, the alkenyl radical, is preferably derived from a polymer prepared from an olefin monomer containing from 2 to 5 carbon atoms. Thus, the alkenyl radical is obtained by polymerizing an olefin containing from 2 to 5 carbon atoms to form a hydrocarbon having a molecular weight ranging from about 400 to 3000. Such olefin monomers are exemplified by ethylene, propylene, 1-butene, 2-butene, isobutene, and mixtures thereof.

The preferred polyalkylene amines used to prepare the succinimides are of the formula:

$$H_2N\text{—}Alk\text{—}\left(\underset{\displaystyle R^2}{\underset{|}{N}}\text{—}Alk\right)_z\text{—}NR^3R^4$$

wherein z is an integer of from 0 to 10 and Alk, R^2, R^3, and R^4 are as defined above.

The alkylene amines include principally methylene amines, ethylene amines, butylene amines, propylene amines, pentylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines and also the cyclic and the higher homologs of such amines as piperazine and amino alkyl-substituted piperazines. They are exemplified specifically by ethylene diamine, triethylene tetraamine, propylene diamine, decamethyl diamine, octamethylene diamine, diheptamethylene triamine, tripropylene tetraamine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, ditrimethylene triamine, 2-heptyl-3-(2-aminopropyl)-imidazoline, 4-methyl imidazoline, N,N-dimethyl-1,3-propane diamine, 1,3-bis(2-aminoethyl)imidazoline, 1-(2-aminopropyl)-piperazine, 1,4-bis(2-aminoethyl)piperazine and 2-methyl-1-(2-aminobutyl)piperazine. Higher homologs such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful.

The ethylene amines are especially useful. They are described in some detail under the heading "Ethylene Amines" in Encyclopedia of Chemical Technology,

Kirk-Othmer, Vol. 5, pp. 898-905 (Interscience Publishers, New York, 1950).

The term "ethylene amine" is used in a generic sense to denote a class of polyamines conforming for the most part to the structure

$$H_2N(CH_2CH_2NH)_aH$$

wherein a is an integer from 1 to 10.

Thus, it includes, for example, ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentamine, pentaethylene hexamine, and the like.

Also included within the term “alkenyl succinimides” are post-treated succinimides such as post-treatment processes involving ethylene carbonate disclosed by Wollenberg, et al., U.S. Patent No. 4,612,132; Wollenberg, et al., U.S. Patent No. 4,746,446; and the like as well as other post-treatment processes each of which are incorporated herein by reference in its entirety.

Preferably, the dispersant component, such as a polyalkylene succinimide, comprises from 2 to 40 weight percent, more preferably 5 to 20 weight percent, and even more preferably 5 to 15 weight percent, of the weight of the oil dispersion of, hydrated alkali metal borate.

Polyalkylene succinic anhydrides or a non-nitrogen containing derivative of the polyalkylene succinic anhydride (such as succinic acids, Group I and/or Group II mono- or di-metal salts of succinic acids, succininate esters formed by the reaction of a polyalkylene succinic anhydride, acid chloride or other derivative with an alcohol, and the like) are also suitable dispersants for use in the compositions of this invention.

The polyalkylene succinic anhydride is preferably a polyisobutenyl succinic anhydride. In one preferred embodiment, the polyalkylene succinic anhydride is a polyisobutenyl succinic anhydride having a number average molecular weight of at least 500, more preferably at least 900 to about 3000 and still more preferably from at least about 900 to about 2300.

In another preferred embodiment, a mixture of polyalkylene succinic anhydrides is employed. In this embodiment, the mixture preferably comprises a low molecular weight polyalkylene succinic anhydride component and a high molecular weight polyalkylene succinic anhydride component. More preferably, the low molecular weight component has a number average molecular weight of from about 500 to below 1000 and the high molecular weight component has a number average molecular weight of from 1000 to about 3000. Still more preferably, both the low and

high molecular weight components are polyisobutenyl succinic anhydrides. Alternatively, various molecular weights polyalkylene succinic anhydride components can be combined as a dispersant as well as a mixture of the other above referenced dispersants as identified above.

As noted above, the polyalkylene succinic anhydride is the reaction product of a polyalkylene (preferably polyisobutene) with maleic anhydride. One can use conventional polyisobutene, or high methylvinylidene polyisobutene in the preparation of such polyalkylene succinic anhydrides. One can use thermal, chlorination, free radical, acid catalyzed, or any other process in this preparation. Examples of suitable polyalkylene succinic anhydrides are thermal PIBSA (polyisobutenyl succinic anhydride) described in U.S. Patent No. 3,361,673; chlorination PIBSA described in U.S. Patent No. 3,172,892; a mixture of thermal and chlorination PIBSA described in U.S. Patent No. 3,912,764; high succinic ratio PIBSA described in U.S. Patent No. 4,234,435; PolyPIBSA described in U.S. Patent Nos. 5,112,507 and 5,175,225; high succinic ratio PolyPIBSA described in U.S. Patent Nos. 5,565,528 and 5,616,668; free radical PIBSA described in U.S. Patent Nos. 5,286,799, 5,319,030, and 5,625,004; PIBSA made from high methylvinylidene polybutene described in U.S. Patent Nos. 4,152,499, 5,137,978, and 5,137,980; high succinic ratio PIBSA made from high methylvinylidene polybutene described in European Patent Application Publication No. EP 355 895; terpolymer PIBSA described in U.S. Patent No. 5,792,729; sulfonic acid PIBSA described in U.S. Patent No. 5,777,025 and European Patent Application Publication No. EP 542 380; and purified PIBSA described in U.S. Patent No. 5,523,417 and European Patent Application Publication No. EP 602 863. The disclosures of each of these documents are incorporated herein by reference in their entirety.

Preferably, the polyalkylene succinic anhydride or other dispersant component comprises from 2 to 40 weight percent, more preferably 5 to 20 weight percent, and even more preferably 5 to 15 weight percent, of the weight of the oil dispersion of hydrated alkali metal borate.

Typically, in the oil dispersion of hydrated alkali metal borate, the hydrated alkali metal borate is in a ratio of at least 2:1 relative to the polyalkylene succinic anhydride or other dispersant, while preferably being in the range of 2:1 to 10:1. In a

more preferred embodiment the ratio is at least 5:1. In another preferred embodiment, mixtures as defined above of the polyalkylene succinic anhydrides are employed.

THE DETERGENT

The oil dispersion of hydrated alkali metal borate employed in the additive compositions of the present invention may optionally contain a detergent. There are a number of materials that are suitable as detergents for the purpose of this invention. These materials include phenates (high overbased or low overbased), high overbased phenate stearates, phenolates, salicylates, phosphonates, thiophosphonates and sulfonates and mixtures thereof. Preferably, sulfonates are used, such as high overbased sulfonates, low overbased sulfonates, or phenoxy sulfonates. In addition the sulfonic acids themselves can also be used.

The sulfonate detergent is preferably an alkali or alkaline earth metal salt of a hydrocarbyl sulfonic acid having from 15 to 200 carbons. Preferably the term "sulfonate" encompasses the salts of sulfonic acid derived from petroleum products. Such acids are well known in the art. They can be obtained by treating petroleum products with sulfuric acid or sulfur trioxide. The acids thus obtained are known as petroleum sulfonic acids and the salts as petroleum sulfonates. Most of the petroleum products which become sulfonated contain an oil-solubilizing hydrocarbon group. Also included within the meaning of "sulfonate" are the salts of sulfonic acids of synthetic alkyl aryl compounds. These acids also are prepared by treating an alkyl aryl compound with sulfuric acid or sulfur trioxide. At least one alkyl substituent of the aryl ring is an oil-solubilizing group, as discussed above. The acids thus obtained are known as alkyl aryl sulfonic acids and the salts as alkyl aryl sulfonates. The sulfonates where the alkyl is straight-chain are the well-known linear alkylaryl sulfonates.

The acids obtained by sulfonation are converted to the metal salts by neutralizing with a basic reacting alkali or alkaline earth metal compound to yield the Group I or Group II metal sulfonates. Generally, the acids are neutralized with an alkali metal base. Alkaline earth metal salts are obtained from the alkali metal salt by metathesis. Alternatively, the sulfonic acids can be neutralized directly with an alkaline earth metal base. The sulfonates can then be overbased, although, for purposes of this invention, overbasing is not necessary. Overbased materials and

methods of preparing such materials are well known to those skilled in the art. See, for example, LeSuer U.S. Pat. No. 3,496,105, issued Feb. 17, 1970, particularly columns 3 and 4.

The sulfonates are present in the oil dispersion in the form of alkali and/or alkaline earth metal salts, or mixtures thereof. The alkali metals include lithium, sodium and potassium. The alkaline earth metals include magnesium, calcium and barium, of which the latter two are preferred.

Particularly preferred, however, because of their wide availability, are salts of the petroleum sulfonic acids, particularly the petroleum sulfonic acids which are obtained by sulfonating various hydrocarbon fractions such as lubricating oil fractions and extracts rich in aromatics which are obtained by extracting a hydrocarbon oil with a selective solvent, which extracts may, if desired, be alkylated before sulfonation by reacting them with olefins or alkyl chlorides by means of an alkylation catalyst; organic polysulfonic acids such as benzene disulfonic acid which may or may not be alkylated; and the like.

The preferred salts for use in the present invention are those of alkylated aromatic sulfonic acids in which the alkyl radical or radicals contain at least about 8 carbon atoms, for example from about 8 to 22 carbon atoms. Another preferred group of sulfonate starting materials are the aliphatic-substituted cyclic sulfonic acids in which the aliphatic substituents or substituents contain a total of at least 12 carbon atoms, such as the alkyl aryl sulfonic acids, alkyl cycloaliphatic sulfonic acids, the alkyl heterocyclic sulfonic acids and aliphatic sulfonic acids in which the aliphatic radical or radicals contain a total of at least 12 carbon atoms. Specific examples of these oil-soluble sulfonic acids include petroleum sulfonic acids, mono- and poly-wax-substituted naphthalene sulfonic acids, substituted sulfonic acids, such as cetyl benzene sulfonic acids, cetyl phenyl sulfonic acids, and the like, aliphatic sulfonic acid, such as paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, etc., cycloaliphatic sulfonic acids, petroleum naphthalene sulfonic acids, cetyl cyclopentyl sulfonic acid, mono- and poly-wax-substituted cyclohexyl sulfonic acids, and the like. The term "petroleum sulfonic acids" is intended to cover all sulfonic acids that are derived directly from petroleum products.

Typical Group II metal sulfonates suitable for use in the present invention include the metal sulfonates exemplified as follows: calcium white oil benzene

sulfonate, barium white oil benzene sulfonate, magnesium white oil benzene sulfonate, calcium dipolypropene benzene sulfonate, barium dipolypropene benzene sulfonate, magnesium dipolypropene benzene sulfonate, calcium mahogany petroleum sulfonate, barium mahogany petroleum sulfonate, magnesium mahogany petroleum sulfonate, calcium triacontyl sulfonate, magnesium triacontyl sulfonate, calcium lauryl sulfonate, barium lauryl sulfonate, magnesium lauryl sulfonate, etc. The concentration of metal sulfonate that may be employed may vary over a wide range, depending upon the concentration of alkali metal borate particles. When present, however, the detergent concentration will generally range from about 0.2 to about 10 weight percent and preferably from about 3 to about 7 weight percent, based on the total weight of the oil dispersion of the hydrated borate. In addition, the compositions of this invention may contain a mixture of both a metal sulfonate and an ashless dispersant, as described above, where the ratio is a factor of achieving the proper stability of the oil dispersion of the hydrated alkali metal borate.

THE OIL OF LUBRICATING VISCOSITY

The lubricating oil to which the hydrated alkali metal borate and the dispersant are added to form the oil dispersion of the hydrated alkali metal borate can be any hydrocarbon-based lubricating oil or a synthetic base oil stock. Likewise, these lubricating oils can be added to the oil dispersion of hydrated alkali metal borate and additive compositions containing them, as described herein, in additional amounts, to form finished oil compositions. The hydrocarbon-based lubricating oils may be derived from synthetic or natural sources and may be paraffinic, naphthenic or aromatic base, or mixtures thereof. The diluent oil can be natural or synthetic, and can be different viscosity grades.

In the oil dispersion of the hydrated alkali metal borate, the lubricating oil typically comprises from about 30 to 70 weight percent, more preferably from about 45 to 55 weight percent, based on the total weight of the oil dispersion of the hydrated alkali metal borate.

In general the oil dispersion of hydrated alkali metal borate is present in the additive composition of the invention in the range of about 10 to 90 weight percent, based on the total weight of the additive composition.

THE OIL DISPERSION OF HEXAGONAL BORON NITRIDE

The additive composition of the present invention further contains an oil dispersion of hexagonal boron nitride.

Hexagonal boron nitride, or h-BN, is a hexagonal, graphite-like form of boron nitride, having a layered structure and planar 6-membered rings of alternating boron and nitrogen atoms. On alternate sheets, boron atoms are directly over nitrogen atoms. Hexagonal boron nitride can be prepared by heating boric oxide, boric acid or boric acid salts with ammonium chloride, alkali cyanides or calcium cyanamide at atmospheric pressure. Hexagonal boron nitride may also be prepared by the reaction of boron trichloride or boron trifluoride with ammonia. A discussion of hexagonal boron nitride can be found, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, Vol. 4, pp. 427-429, John Wiley and Sons, New York, 1992.

Generally, the hexagonal boron nitride will have a mean particle size of less than 1 micron. Preferably, the hexagonal boron nitride will have a particle size distribution wherein 90% or greater of the particles are less than about 0.5 microns (500 nanometers, nm), with a preferred mean particle size of less than about 0.3 microns (300 nm).

Typically, the oil dispersion of the hexagonal boron nitride will contain about 1 to about 50 weight percent of the hexagonal boron nitride, preferably about 1 to about 20 weight percent, and more preferably about 5 to about 15 weight percent, based on the total weight of the oil dispersion.

Preferably, the oil dispersion of the hexagonal boron nitride will contain a surfactant as a stabilizer for the oil dispersion. Typical surfactants for use as a stabilizer include ethylene – propylene copolymers, or terpolymers of ethylene, propylene and an unconjugated dienes commonly known as ethylene-propylene-diene terpolymer, ethylene-propylene copolymers grafted with a nitrogen-containing vinyl functionality selected from the group consisting of N-vinyl pyrrollidone and N-vinyl pyridine, and the like. The ethylene-propylene copolymer generally has an average molecular weight in the range of about 22,000 to 200,000. A preferred surfactant is ethylene – propylene copolymer which has substantially equal proportions of ethylene and propylene monomers and an average molecular weight of from 22,000 to about 40,000. When present, the surfactant concentration in the oil dispersion of hexagonal

boron nitride will typically range from about 0.1 to about 25 weight percent, preferably from about 2 to about 7 weight percent, and more preferably from about 3.0 to about 5.0 weight percent, based on the total weight of the oil dispersion of hexagonal boron nitride.

The lubricant oil used to prepare the oil dispersion of the hexagonal boron nitride may be selected from the same group of natural or synthetic lubricating oils described above for use in preparing the oil dispersion of the hydrated alkali metal borate, but other carrier fluids have been found to be satisfactory, including vegetable oils such as rapeseed oil; liquid hydrocarbons such as aliphatic and aromatic naphthas and mixtures thereof; synthetic lubricant fluids such as polyalphaolefins, polyglycols, diester fluids, and mixtures of these liquids. Moreover, the oil used in forming the oil dispersion of hexagonal boron nitride may be the same as, or different from, the lubricant oil employed in preparing the oil dispersion of hydrated alkali metal borate. Typical oils for preparing the oil dispersion of hexagonal boron nitride include the Group I and Group II base oils, such as 150 solvent neutral petroleum oil.

In general, the oil dispersion of hexagonal boron nitride is present in the additive composition of the invention in the range of about 10 to 90 weight percent, based on the total amount of the additive composition.

FORMULATIONS

The additive compositions of the present invention containing oil dispersions of alkali metal borate and hexagonal boron nitride (as described hereinabove) may be blended further with additional additives to form additive packages containing the present additive compositions. These additive packages typically comprise from about 10 to 80 weight percent of the additive composition of the present invention described above and from about 90 to 20 weight percent of one or more of conventional additives selected from the group consisting of ashless dispersants (0-10%), detergents (0-5%), sulfurized hydrocarbons (0-40%), dialkyl hydrogen phosphates (0-15%), zinc dithiophosphates (0-20%), alkyl ammonium phosphates and/or thio- dithiophosphates (0-20%), phosphites (0 to 10%) fatty acid esters of polyalcohols (0-10%), 2,5-dimercaptothiadiazole (0-5%), benzotriazole (0-5%), dispersed molybdenum disulfide (0-5%), foam inhibitors (0-2%), and imidazolines (0-

10%) and the like wherein each weight percent is based on the total weight of the composition.

Fully formulated finished oil compositions of this invention can be formulated from these additive packages upon further blending with an oil of lubricating viscosity. Preferably, the additive package described above is added to an oil of lubricating viscosity in an amount of from about 1 to 20 weight percent, preferably about 2 to 15 weight percent, to provide for the finished oil composition wherein the weight percent of the additive package is based on the total weight of the composition.

A variety of other additives can be present in lubricating oils of the present invention. These additives include antioxidants, rust inhibitors, corrosion inhibitors, extreme pressure agents, antifoam agents, other anti-wear agents, and a variety of other well-known additives in the art.

EXAMPLES

The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate the present invention, they are not intended to limit it.

EXAMPLE 1

The additive composition of the present invention was evaluated in a lubricating oil for its anti-sticking properties following a test using an SAE No. 2 bench, which evaluates transmission fluids during synchronization. The friction pairs used in this bench comprised a brass synchronizer ring and a steel gear cone.

During each cycle of the test, the cone is rotating, at a given speed, then the ring moves along the axis of the cone for its braking until it is blocked. At the end of each cycle, the ring is disengaged.

If sticking occurs, a sticking torque is measured when rotation of the cone is resumed. During the test, the lubricating oil and the metal parts are heated to a temperature between about 60°C and 90°C. The contact pressure is about 20 MPa and the initial sliding speed is 1.6 m/s.

The anti-sticking coefficient for this test was calculated as follows:

$$\text{Anti-sticking coefficient} = 1 - \frac{(\text{No. of cycles with sticking})}{(\text{Total No. of cycles in test})}$$

Accordingly, an anti-sticking coefficient of 0 indicates the presence of cone on ring sticking during every cycle of the test. Conversely, an anti-sticking coefficient of 1 indicates no sticking at all was observed over the entire duration of the test. Thus, the higher the anti-sticking coefficient, up to a maximum of 1, the better the anti-sticking performance of the lubricating oil.

The test lubricating oil compositions were formulated as follows:

Lubricant Composition 1

A lubricant composition was prepared containing the following:

(a) 7 weight percent of an oil dispersion of hydrated potassium triborate, wherein the oil dispersion contained about 30 weight percent of the hydrated potassium triborate, dispersed in a 150 N neutral oil;

(b) 10 weight percent of an oil dispersion of hexagonal boron nitride, wherein the oil dispersion contained about 10 weight percent of the hexagon boron nitride solids, dispersed in a 150 N neutral oil containing a stabilizing agent; and

(c) 83 weight percent of a 50/50 mixture of neutral oil (150N plus 600N) and a synthetic polyalphaolefin oil.

Lubricant Composition 2

The lubricant composition 2 was prepared containing the following:

(a) 7 weight percent of an oil dispersion of hydrated potassium triborate, wherein the oil dispersion contained about 30 weight percent of the hydrated potassium triborate, dispersed in a 150 N neutral oil;

(b) 5 weight percent of an oil dispersion of hexagonal boron nitride, wherein the oil dispersion contained about 10 weight percent of the hexagon boron nitride solids, dispersed in a 150 N neutral oil containing a stabilizing agent; and

(c) 88 weight percent of a 50/50 mixture of neutral oil (150N plus 600N) and a synthetic polyalphaolefin oil.

Lubricant Composition 3

The lubricant composition 3 was prepared containing the following:

(a) 7 weight percent of an oil dispersion of hydrated potassium triborate, wherein the oil dispersion contained about 30 weight percent of the hydrated potassium triborate, dispersed in a 150 N neutral oil;

(b) 2.5 weight percent of an oil dispersion of hexagonal boron nitride, wherein the oil dispersion contained about 10 weight percent of the hexagon boron nitride solids, dispersed in a 150 N neutral oil containing a stabilizing agent; and

(c) 90.5 weight percent of a 50/50 mixture of neutral oil (150N plus 600N) and a synthetic polyalphaolefin oil

Lubricant Composition A (comparative)

A lubricating composition was prepared containing the following:

(a) 7 weight percent of an oil dispersion of hydrated potassium triborate, wherein the oil dispersion contained about 30 weight percent of the hydrated potassium triborate, dispersed in a 150 N neutral oil; and

(b) 93 weight percent of a 50/50 mixture of neutral oil (150N plus 600N) and a synthetic polyalphaolefin oil.

Lubricant Composition B (comparative)

A lubricating composition was prepared containing the following:

(a) 10 weight percent of an oil dispersion of hexagonal boron nitride, wherein the oil dispersion contains about 10 weight percent of the hexagonal boron nitride solids, dispersed in a 150 N neutral oil containing a stabilizing agent; and

(b) 90 weight percent of a 50/50 mixture of neutral oil (150N plus 600N) and a synthetic polyalphaolefin oil.

The above lubricant compositions were evaluated for anti-sticking performance in the synchronization test described above. A base oil containing a 50/50 mixture of 150N and 600N neutral oil, with no additives, was also tested. The results of this evaluation are shown in Table 1.

Table 1

Sample	No. of Cycles with Cone on Ring Sticking	Total No. of Cycles	Anti-sticking coefficient
Base oil	5000	5000	0
Comparative Composition A	8100	8100	0
Comparative Composition B	6600	6600	0
Composition 1	1200	7500	0.84
Composition 2	1600	8710	0.82
Composition 3	300	10560	0.97

The above data demonstrates that the additive composition of the present invention provides significant anti-sticking performance and shows a marked improvement over the comparative compositions.

From the foregoing description, various modifications and changes in the above-described invention will occur to those skilled in the art. All such modifications coming within the scope of the appended claims are intended to be included therein.